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## Common tangent plane in mixed-gas adsorption

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### Abstract

The minimisation of the distance function between the Gibbs energy of mixing and its common tangent plane (or line) is applied to adsorbed solutions. A specific algorithm to deal with the associated bilevel programming problem is presented and discussed. This approach is validated with experimental data and ideal adsorbed solution theory calculations for an ideal case and with experimental data for two non-ideal cases at low and high pressure. While the presently adopted non-ideal formulation provides solutions fulfilling only the necessary condition for equilibrium, the common tangent plane approach proposed in this paper enables the direct evaluation of the necessary and sufficient solution.

Keywords: Gibbs energy of mixing; Adsorption thermodynamics; Common tangent plane; Double tangent plane; Azeotropy; Adsorbed solution theory

### 1. Introduction

The adsorbed solution theory (AST) interprets gas-adsorbate equilibrium similarly to vapour-liquid equilibrium (VLE) [1]. The theory states the presence of two partially miscible phases such as a bulk gas phase and an adsorbed phase. There are no thermodynamic flaws in such an approach in the case of single component adsorption while, as discussed in [2], for the case of multi-component mixture adsorption, the iso-reduced-grand-potential condition is mandatory to make the theory thermodynamically consistent. The necessity of such an additional condition with respect to VLE results from the phase rule applied to adsorption equilibrium [3]. In the simplest case adsorption thermodynamics of multicomponent mixtures is assumed ideal with the bulk gas phase being an ideal gas and the adsorbed phase being an ideal solution. The ideal adsorption solution theory (IAST) is based on these assumptions [3], where the equilibrium is described by the pseudo Raoult's law:

$$P_{bulk} y_i = P_i^0 x_i \quad i = 1, 2, \dots, NC \quad (1)$$

with

$$\sum_i^{NC} x_i = 1 \quad (2)$$

where  $P_{bulk}$  is the pressure in the bulk gas phase,  $y_i$  is the molar fraction of the component  $i$  in the bulk gas phase,  $x_i$  is the molar fraction of the component  $i$  in the adsorbed phase,  $NC$  is the total number of components and  $P_i^0$  is the surface pressure of the component  $i$ .

The iso-reduced-grand-potential condition states that each component in the adsorbed phase has the same reduced grand potential at equilibrium. This last condition is expressed for the ideal case as follows:

$$\psi_i = \int_0^{P_i^0} n_i d(\ln P_i) \quad i = 1, 2, \dots, NC \quad (3)$$

$$\psi_i = const \quad i = 1, 2, \dots, NC \quad (4)$$

where  $\psi_i$  [mol/kg] is the reduced grand potential of the component  $i$  and  $n_i$  is the absolute amount adsorbed for the pure component  $i$  [mol/kg], extensively described in [4, 5].

By specifying the bulk gas pressure ( $P_{bulk}$ ), the equilibrium temperature ( $T$ ) and composition of the multicomponent gaseous mixture in the bulk phase ( $y_i$ ), the composition of the multicomponent mixture in the adsorbed phase can be calculated solving the system of eqns (1)-(4). This interpretation is successful in several adsorption systems which can be assumed ideal.

For a more general case, activity coefficients and fugacity coefficients must be introduced in eq. (1) to take into account non-ideal behaviour in both phases. Thus eq. (1) and eq. (3) become:

$$P_{bulk} y_i \phi_i = \phi_i^0 P_i^0 x_i \gamma_i \quad i = 1, 2, \dots, NC \quad (5)$$

$$\psi_i = \int_0^{f_i^0} n_i d(\ln f_i) \quad i = 1, 2, \dots, NC \quad (6)$$

where  $\phi_i$  and  $\gamma_i$  are respectively the fugacity and activity coefficients of component  $i$ ,  $\phi_i^0$  is the fugacity coefficient of the pure component  $i$  in the adsorbed phase and  $f_i = P_{bulk} y_i \phi_i$  is the fugacity of the component  $i$  in the bulk gas phase.

Eqns (5) and (6) need additional models for the evaluation of fugacity and activity coefficients. While the fugacity coefficients can be calculated using the extensive thermodynamic work on specific equations of state, the activity coefficients cannot be predicted from liquid state models because they do not include the interaction with the solid adsorbent, which is implicit in the definition of the reduced grand potential [5, 6]. The non-ideal formulation of the AST through the system of eqns (2, 4-6), provides solutions fulfilling only the necessary condition for equilibrium. In general, multiple solutions exist for the above system of equations and convergence to a specific solution depends on the choice of the initial guess. Despite this, strongly non-ideal adsorption systems are reported rarely in the open literature and the above formulation converges to the physically correct solution.

Rigorously, only the common tangent plane (or line) of the molar Gibbs energy of mixing ( $\Delta g_{mix}$ ) or alternatively the global minimisation of Gibbs energy locate equilibrium compositions which fulfil the necessary and sufficient condition at the same time.

The present work shows applications of the common tangent plane (CTP) approach to ideal and non-ideal adsorption equilibria in case of binary system.

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## 2. Gibbs energy of mixing for ideal adsorbed solutions

The definition of ideal solution can be given according to Lewis-Randall or Raoult's law. These two definitions are contradictory in some aspects as pointed out in [7, 8]. It is essentially not possible to have the same definition of ideal solution that satisfies Raoult's law and has a simple expression of the ideal-mixture property changes on mixing at the same time. According to the Lewis-Randall definition, in an ideal solution the fugacities of the components at constant temperature and pressure follow:

$$f_i = w_i f_i^0 \quad i = 1, 2, \dots, NC \quad (7)$$

where  $f_i^0$  is the fugacity of pure component  $i$  at the system temperature and pressure and  $w_i$  is the mole fraction of component  $i$  in the specific phase considered. Accordingly, the molar Gibbs energy of mixing is represented by:

$$\Delta g_{mix} = RT \sum_i^{NC} w_i \ln \left( \frac{f_i}{f_i^0} \right) \quad (8)$$

Applying eq. (7) the following equation is derived:

$$\Delta g_{mix} = RT \sum_i^{NC} w_i \ln(w_i) \quad (9)$$

By applying eq. (7), it is demonstrated that a Raoult's law solution in equilibrium with an ideal gas does not match the Lewis-Randall rule [7]. This is due to the need to choose two different reference states for the pure components in order to describe correctly the dependency of  $\Delta g_{mix}$  on composition. This also leads to a different expression of  $\Delta g_{mix}$  for each phase. The Lewis-Randall ideal solution definition can be readily extended to adsorbed solutions. The only aspect to carefully evaluate is the selection of the reference state for the fugacities in eq. (8) which are crucial for calculating the correct  $\Delta g_{mix}$ . In analogy with the considerations reported in [8, 9] for VLE, and limiting for sake of clarity the study to a binary system at a fixed temperature and ideal in both phases,  $P_{bulk}$  will be located between the equilibrium surface pressures ( $P_i^0$ ) of the components (Fig. 1). Considering component 1 as the most strongly adsorbed component and component 2 as the less strongly adsorbed component, the first one will have a higher reduced grand potential curve than the second one and for this reason its reference state will be in the adsorbed phase which is its more stable phase. Conversely, the less strongly adsorbed component will have the reference state in the gas phase. This result leads to the following equations:

$$\frac{g}{RT} = \begin{cases} \frac{g_{mix,ads}}{RT} = x_1 \ln(x_1) + x_2 \ln\left(\frac{P_2^0 x_2}{P_{tot}}\right) \\ \frac{g_{mix,gas}}{RT} = y_1 \ln\left(\frac{P_{tot} y_1}{P_1^0}\right) + y_2 \ln(y_2) \end{cases} \quad (10)$$

where  $g_{mix,ads}$  and  $g_{mix,gas}$  compose the resulting  $g$  function.  $\Delta g_{mix}$  will be a piecewise function including the  $g$  function except in the linear region identified by the CTP. Fig. 1 is illustrative of the above presented case and it is based on the data reported in [10]. It represents the Nitrogen/Oxygen binary system adsorbed on zeolite 5A at 298 K. Nitrogen (1) is the most strongly adsorbed component and Oxygen (2) is the less strongly adsorbed component.  $P_{bulk}$  is always between the surface pressures of the two components. The reference states are assumed to be the adsorbed phase for the component 1 as it is stable in the adsorbed phase and in the bulk gas phase for the component 2 as it is more stable in the bulk gas phase

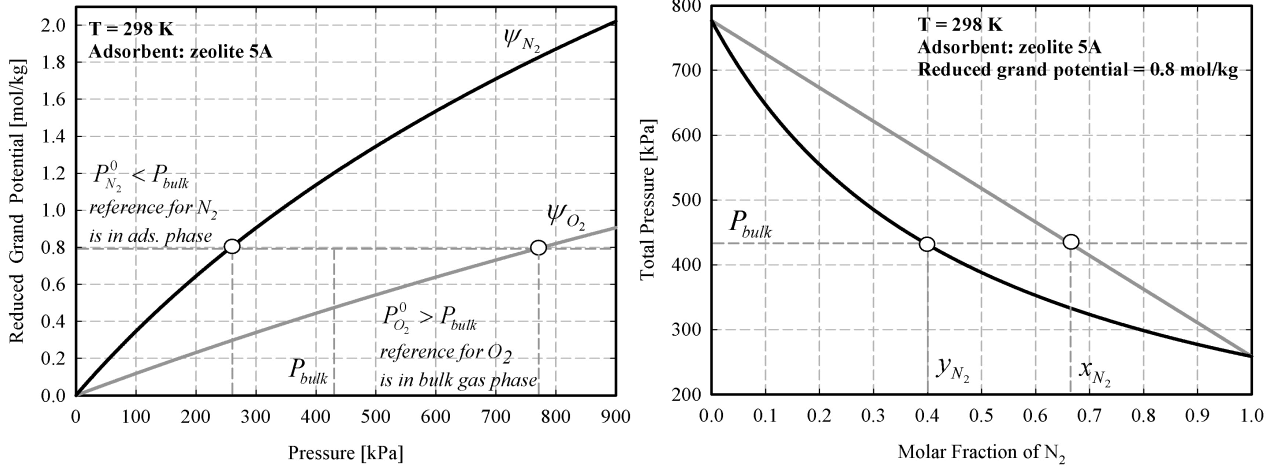


Figure 1: Reduced grand potential diagram (left) and  $(P,x,y)$  diagram (right) for Nitrogen/Oxygen binary system on zeolite 5A at 298 K. Reference states for the two components must be selected on the basis of  $P_{bulk}$  and  $P_i^0$  mutual position.

With the reference states of eq. (10),  $\Delta g_{mix}$  approaches a zero value when the molar fraction of component 1 approaches zero or one (Fig. 2). The first critical aspect in the formulation above consists of the selection of the correct mutual position of the surface pressures and bulk gas phase pressure, which is usually unknown before the calculation. This makes it impossible to set-up the reference states a-priori, without a preliminary check. Fortunately,  $\Delta g_{mix}$  is a state function and this makes the CTP approach independent from the selection of the reference states. Considering for example the bulk gas phase as a reference state for both the components, the resulting equation is:

$$\frac{g}{RT} = \begin{cases} \frac{g_{mix,ads}}{RT} = x_1 \ln\left(\frac{P_1^0 x_1}{P_{tot}}\right) + x_2 \ln\left(\frac{P_2^0 x_2}{P_{tot}}\right) \\ \frac{g_{mix,gas}}{RT} = y_1 \ln(y_1) + y_2 \ln(y_2) \end{cases} \quad (11)$$

Fig. 2 illustrates that the CTP calculated from eq. (10) and eq. (11) leads to the same equilibrium molar fractions. Thus, in order to simplify the treatment, in this work the reference states will always be taken in bulk gas phase like in eq. (11).

Finally, in the ideal case, the total number of adsorbed moles  $n_{tot}$  is calculated from:

$$\frac{1}{n_{tot}} = \sum_{i=1}^{NC} \left( \frac{x_i}{n_i(P_i^0)} \right) \quad (12)$$

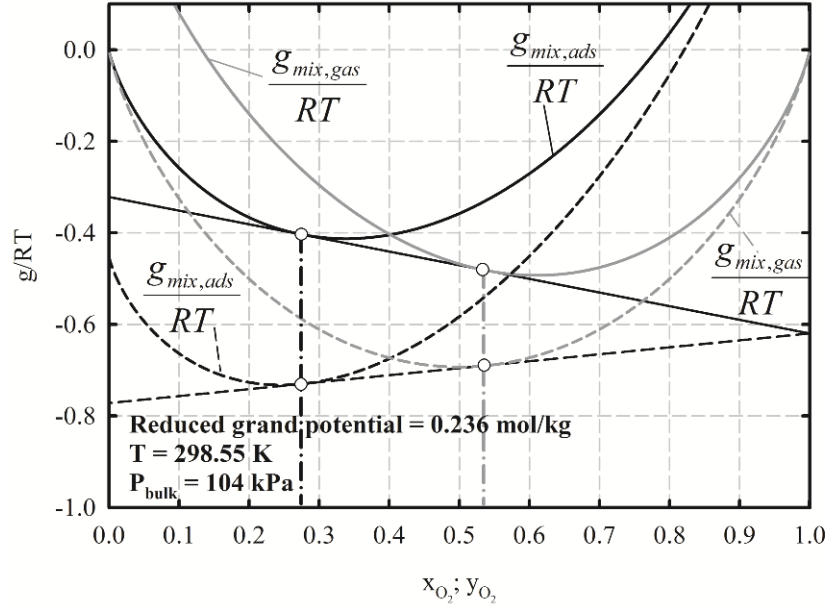


Figure 2: Common tangent plane for Nitrogen/Oxygen mixture on zeolite 5A [10] at 298.55 K, 104 kPa and  $y_{O_2}=0.538$ . Solid lines are from eq. (10), dashed lines are from eq. (11).

### 3. Minimisation of the tangent distance function

In adsorption equilibria the minimisation of the CTP distance function has an additional challenge compared with VLE because  $\Delta g_{\text{mix}}$  is a function of both the equilibrium reduced grand potential and equilibrium compositions. For this reason the minimisation of the CTP distance function for adsorption is a bilevel programming problem. A bilevel programming problem is a hierarchical problem where a first outer optimization problem is constrained by an inner second one [11]. The outer level is devoted to the minimisation of one objective function based on the iso-reduced grand potential condition, while the inner level minimises the CTP distance function at the reduced grand potential calculated by the outer level. The algorithm is illustrated in the flow chart depicted in Fig. 3. The necessary data are the molar fractions  $y_i$  in the bulk phase, the equilibrium pressure  $P_{\text{bulk}}$  and the equilibrium temperature  $T$ . Considering a binary system, the algorithm operates according to the following steps:

- 1) The first iteration is performed providing an initial guess for the reduced grand potential  $\psi_{\text{eq}}$  and calculating the corresponding surface pressures  $P_i^0(\psi_{\text{eq}})$ . These values are introduced in eq.(11), which, after the substitution  $x_2=1-x_1$ , represents a system of two equations in two unknowns ( $x_1, y_1$ ).  $y_{1,\text{exp}}$  is the composition of the bulk phase and a tangent can be built upon  $g_{\text{mix,gas}}/RT$ . Finally, the distance function between this tangent and eq. (11) can be evaluated. The distance function is:

$$DF(x_1, y_1, \psi_{\text{eq}}) = \left| \frac{g(x_1, y_1, \psi_{\text{eq}})}{RT} - \tan \Big|_{y_1=y_{1,\text{exp}}} \right| \quad (13)$$

where  $\tan$  is the tangent of  $g_{\text{mix,gas}}/RT$ , calculated at the composition  $y_{1,\text{exp}}$ .

- 2) The minimum absolute value of eq. (13) is evaluated and this minimum locates the position of  $x_{1,\text{iter}}$ .  $x_{1,\text{iter}}$  is the calculated composition of component 1 in the adsorbed phase. If  $\text{Min}(DF(x_{1,\text{iter}}, y_1, \psi_{\text{eq}})) > 10^{-6}$ , the reduced grand potential of this iteration is not accepted and the algorithm goes back to the outer level.
- 3) The outer level minimises the same distance function of eq. (13) changing the value of the equilibrium reduced grand potential  $\psi_{\text{eq}}$  in order to obtain the lowest value of eq. (13).
- 4) The algorithm terminates when  $\text{Min}(DF(x_{1,\text{iter}}, y_1, \psi_{\text{eq}})) < 10^{-6}$ . The minimum of  $DF$  locates the equilibrium value of  $x_1$  and the outer level determines  $\psi_{\text{eq}}$ .

In all the cases considered in the present work, the Nelder-Mead algorithm [12] has been adopted both for the inner and the outer levels. The presented algorithm is representative of the AST applied in a predictive way. When the same theory is used in a correlative way then  $y_1$  should not be specified among the given values but derived directly from the CTP. In this case the outer level is formulated to minimize the error (in both phases) between experimental and calculated compositions.

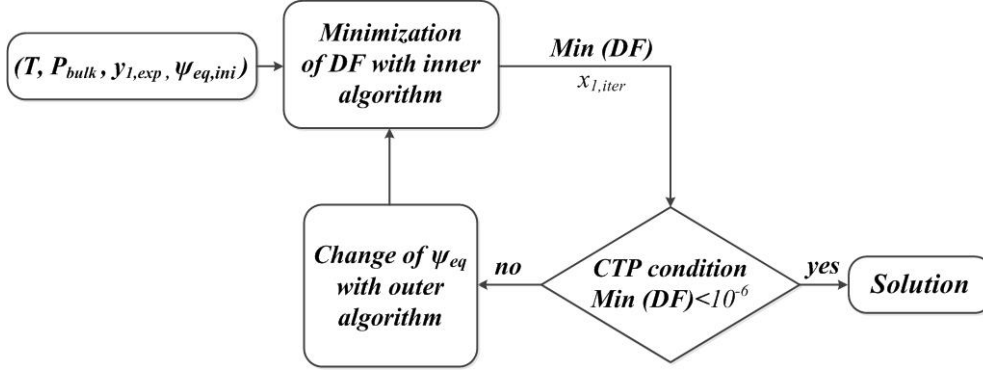


Figure 3: Algorithm for the calculation of the common tangent plane of  $\Delta g_{\text{mix}}$  at the equilibrium reduced grand potential  $\psi_{\text{eq}}$

#### 4. Validation of common tangent approach with experimental data and Raoult's law IAST

Experimental data concerning adsorption of Nitrogen(1)/Oxygen(2) binary system on zeolite 5A at low pressure [10] have been considered for comparison of the results from Raoult's law IAST proposed in [3] and the CTP approach proposed in this paper. Langmuir isotherm parameters are reported in Table 1.

Table 1: Parameters of Langmuir and Dual-site Langmuir isotherms for adsorption

	Temperature [K]	$q_{s1}$ [mol/kg]	$b_1$ [1/kPa]	$q_{s2}$ [mol/kg]	$b_2$ [1/kPa]	Ref
Nitrogen <sup>1</sup>	298.55	2.114	0.001756	--	--	[10]
Oxygen <sup>1</sup>	298.55	2.313	0.000524	--	--	[10]
Carbon Dioxide <sup>2</sup>	293.00	2.166	5.803367	4.011	0.093840	[13]
Propane <sup>3</sup>	293.00	3.296	1.188920	--	--	[13]
Methane <sup>4</sup>	298.00	9.307	0.000429	1.557	0.019832	[18]
Carbon Monoxide <sup>4</sup>	298.00	7.999	0.000346	0.470	0.026290	[18]

Note:

<sup>1</sup> data fitted over the pressure using Langmuir isotherm on zeolite 5A

<sup>2</sup> data fitted over the pressure using Dual-site Langmuir isotherm on zeolite 13X

<sup>3</sup> data fitted over the pressure using Langmuir isotherm on zeolite 13X

<sup>4</sup> data fitted over the fugacity using Dual-site Langmuir isotherm on activated carbon NoritR1

Table 2 summarises the results of the comparison and shows complete agreement between the values calculated with the two different methods. Small differences are due to different approximations adopted by the numerical solvers used in the two methods. These identical results are a further proof of the correctness of the proposed framework for ideal adsorption equilibrium. Fig. 2 shows the CTPs obtained applying the method previously described to one of the experimental conditions of Table 2.

Table 2: Data for Nitrogen(1)/Oxygen(2) adsorption on zeolite 5A [10] at 298.55K. Comparison among experimental data, results of common tangent plane approach and of Raoult's law IAST.

$P_{\text{bulk}}$ [kPa]	$y_{1,\text{exp}}$	$x_{1,\text{exp}}$	$n_{\text{tot,exp}}$ [mol/kg]	Common tangent plane approach				Raoult's law IAST					
				$x_1$	$n_{\text{tot}}$ [mol/kg]	$\psi_{\text{eq}}$ [mol/kg]	$P_1^0$ [kPa]	$P_2^0$ [kPa]	$x_1$	$n_{\text{tot}}$ [mol/kg]	$\psi_{\text{eq}}$ [mol/kg]	$P_1^0$ [kPa]	$P_2^0$ [kPa]
104	0.632	0.847	0.262	0.840	0.259	0.275	78.22	239.71	0.840	0.259	0.275	78.22	239.70
104	0.635	0.847	0.263	0.842	0.259	0.276	78.43	240.35	0.842	0.259	0.276	78.43	240.34
104	0.347	0.621	0.199	0.620	0.199	0.208	58.19	178.79	0.620	0.199	0.208	58.19	178.78
104	0.100	0.260	0.142	0.255	0.144	0.148	40.80	125.62	0.255	0.144	0.148	40.79	125.62
104	0.811	0.928	0.298	0.929	0.294	0.316	90.77	277.76	0.929	0.294	0.316	90.76	277.74
104	0.787	0.915	0.294	0.919	0.289	0.311	89.09	272.67	0.919	0.289	0.311	89.08	272.64
104	0.462	0.724	0.223	0.725	0.223	0.236	66.28	203.42	0.725	0.223	0.236	66.28	203.42
104	0.225	0.472	0.173	0.472	0.172	0.179	49.61	152.57	0.472	0.172	0.179	49.61	152.57
104	0.223	0.474	0.174	0.469	0.172	0.178	49.47	152.14	0.469	0.172	0.178	49.47	152.14
300	0.657	0.848	0.622	0.852	0.618	0.729	231.26	696.69	0.852	0.618	0.728	231.26	696.66
300	0.229	0.478	0.439	0.475	0.437	0.484	144.76	440.22	0.475	0.437	0.484	144.76	440.21
300	0.099	0.254	0.376	0.251	0.371	0.404	118.32	360.89	0.251	0.371	0.404	118.29	360.92
300	0.353	0.628	0.501	0.623	0.494	0.558	169.91	515.24	0.623	0.494	0.558	169.91	515.23
400	0.664	0.850	0.761	0.855	0.756	0.930	310.57	928.21	0.855	0.756	0.930	310.57	928.15
400	0.100	0.257	0.478	0.252	0.471	0.525	158.57	481.45	0.252	0.471	0.525	158.57	481.45

The Nitrogen/Oxygen binary system is ideal under the specific conditions considered (Fig. 4) and the maximum absolute errors on molar fractions and number of total adsorbed moles are respectively 2.0% and 1.6%. These results are the basis for non-ideal cases where excess Gibbs energy models have to be added.

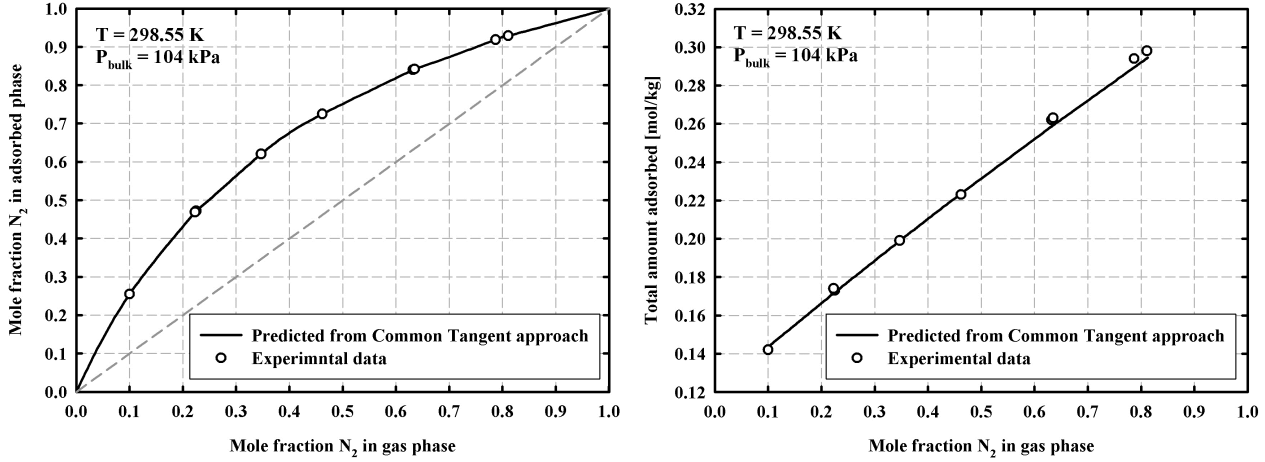


Figure 4: Comparison between experimental data and results from common tangent plane for binary system Nitrogen/Oxygen on zeolite 5A [10]

### 5. Common tangent approach for non-ideal adsorption at low pressure

Adsorption of the Carbon Dioxide(1)/Propane(2) binary system on zeolite 13X exhibits an azeotrope and it has been extensively studied introducing a model for the excess Gibbs energy [14]. Isotherms parameters are reported in Table 1. This system forms an azeotrope in a specific range of conditions and the excess Gibbs energy ( $g_{ex}$ ) follows the ABC equation [15] with parameters  $A = -11.5$  kJ/mol;  $B = 0.01453$  kJ/(mol K) and  $C = 0.096$  kg/mol. The ABC equation for a binary system is given by:

$$g_{ex} = (A + BT)x_1x_2(1 - e^{-C\psi}) \quad (14)$$

In order to consider a fully non-ideal adsorption, fluid-fluid and fluid-solid interactions must be included. Fluid-solid interactions can be taken into account adding an excess Gibbs energy term to eq. (11). Fluid-fluid interactions are considered including bulk gas phase fugacities and the reduced grand potential expressed by eq. (6). Thus, the function  $g/RT$  becomes:

$$\frac{g}{RT} = \begin{cases} \frac{g_{mix,ads}}{RT} = x_1 \ln \left( \frac{\phi_1^0 P_1^0 x_1}{P_{tot}} \right) + x_2 \ln \left( \frac{\phi_2^0 P_2^0 x_2}{P_{tot}} \right) + \frac{g_{ex}}{RT} \\ \frac{g_{mix,gas}}{RT} = y_1 \ln \left( \frac{f_1}{f_{1,pure}} \right) + y_2 \ln \left( \frac{f_2}{f_{2,pure}} \right) \end{cases} \quad (15)$$

where  $f_i$  is the fugacity of component  $i$  in the mixture and  $f_{i,pure}$  is the fugacity of the pure component. The Carbon Dioxide(1)/Propane(2) binary system in the conditions of Table 4 is moderately non-ideal and for this reason the Virial equation of state truncated at the second Virial coefficient has been used.

Solving the integral of eq. (6), the reduced grand potential for this case is:

$$\begin{aligned} \psi_i = & q_{s1,i} \ln(1 + b_{1,i} P_i^0) + q_{s2,i} \ln(1 + b_{2,i} P_i^0) + \\ & + \frac{B_{ii}}{RT} \left( q_{s1,i} P_1^0 + q_{s2,i} P_2^0 - \frac{q_{s1,i} \ln(1 + b_{1,i} P_i^0)}{b_{1,i}} - \frac{q_{s2,i} \ln(1 + b_{2,i} P_i^0)}{b_{2,i}} \right) \quad i = 1, 2, \dots, NC \end{aligned} \quad (16)$$

where  $B_{ii}$  is the second virial coefficient for the pure component  $i$ . Fugacities of the two components in mixture are:

$$\begin{aligned} \ln(f_1) = & \frac{P_{bulk}}{RT} [B_{11} + y_2^2 (2B_{12} - B_{11} - B_{22})] \\ \ln(f_2) = & \frac{P_{bulk}}{RT} [B_{22} + y_1^2 (2B_{12} - B_{11} - B_{22})] \end{aligned} \quad (17)$$

where  $B_{12}$  is the cross second Virial coefficient. Table 3 reports the coefficients of the three temperature-dependent linear correlations used for the calculation of the Virial coefficients in eq. (17).

Table 3: Coefficients of the linear correlations ( $a_0 + a_1 T$ ) used for Virial coefficients for the Carbon Dioxide(1)/Propane(2) binary system.

	$a_0$	$a_1$
$B_{11}$ [m <sup>3</sup> /mol]	$-4.125 \cdot 10^{-4}$	$9.707 \cdot 10^{-7}$
$B_{12}$ [m <sup>3</sup> /mol]	$-4.692 \cdot 10^{-4}$	$9.894 \cdot 10^{-7}$
$B_{22}$ [m <sup>3</sup> /mol]	$-1.248 \cdot 10^{-3}$	$2.876 \cdot 10^{-6}$

Note:  $B_{11}$  and  $B_{22}$  are regressed in the temperature range 291-301 K on data from [16],  $B_{12}$  is regressed in the temperature range 303-377 K on data from [17].

In this case the number of total adsorbed moles is derived as follows:

$$\frac{1}{n_{tot}} = \left( \frac{1}{n} \right)^{ex} + \sum_{i=1}^{NC} \left( \frac{x_i}{n_i (\phi_i^0 P_i^0)} \right) \quad (18)$$

with:

$$\left( \frac{1}{n} \right)^{ex} = \frac{\partial (g_{ex} / RT)}{\partial \psi} \bigg|_{T,x} \quad (19)$$

Table 4 shows that CTP approach matches all the experimental data reported in [13]. For sake of clarity, although the data are reported as a function of  $P_{bulk}$ , the isotherm parameters in Table 1 were obtained regressing the adsorbed amount against the fugacity. The maximum errors with experimental data are  $-4.2\%$  for the case of adsorbed phase mole fraction and  $-4.9\%$  for the case of total adsorbed moles, requiring an average number of 2156 iterations. Eventually, Fig. 5 shows the presence of an azeotropic aggregation state and the respective common tangent lines locating the equilibrium compositions at constant reduced grand potential,.

Table 4: Comparison between experimental data in [13] and results from common tangent plane approach for adsorption of Carbon Dioxide(1)/Propane(2) binary system on zeolite 13X

T [K]	$P_{bulk}$ [kPa]	$n_{tot,exp}$ [mol/kg]	$y_{1,exp}$	$x_{1,exp}$	$x_{1,calc}$	$x_{1,error}$	$n_{tot,calc}$ [mol/kg]	$n_{tot,error}$	$\gamma_1$	$\gamma_2$	$\psi_{eq}$ [mol/kg]	$I_{inner}$	$I_{outer}$
294.07	47.91	5.35	0.966	0.969	0.949	2.1	5.35	0.0	0.994	0.107	19.2	63.5	34
294.06	53.48	5.43	0.966	0.970	0.951	2.0	5.41	0.4	0.994	0.103	19.7	59.0	34
294.34	64.05	5.49	0.930	0.946	0.921	2.7	5.42	1.4	0.984	0.115	20.8	63.4	34
294.50	70.20	5.55	0.929	0.948	0.924	2.6	5.45	1.8	0.985	0.112	21.3	63.1	34
294.63	83.22	5.59	0.888	0.927	0.902	2.8	5.45	2.6	0.975	0.121	22.2	64.6	33
293.85	10.26	4.19	0.812	0.826	0.796	3.7	4.23	-0.8	0.919	0.277	12.0	57.2	32
293.78	14.35	4.38	0.741	0.786	0.759	3.5	4.44	-1.5	0.883	0.290	13.5	60.9	32
293.73	17.80	4.51	0.745	0.794	0.766	3.7	4.57	-1.4	0.885	0.272	14.4	68.1	30
293.77	26.14	4.64	0.659	0.764	0.735	3.9	4.70	-1.4	0.849	0.284	16.1	61.1	32
293.81	32.52	4.76	0.660	0.774	0.744	4.0	4.80	-0.9	0.855	0.266	17.2	66.5	33
293.78	44.82	4.83	0.584	0.753	0.724	4.0	4.84	-0.3	0.829	0.275	18.5	99.0	34
293.52	10.97	4.04	0.396	0.582	0.582	0.0	4.07	-0.9	0.705	0.507	11.7	60.5	32
293.51	14.19	4.16	0.406	0.599	0.594	0.8	4.21	-1.2	0.708	0.476	12.8	68.2	33
293.98	27.49	3.47	0.024	0.203	0.202	0.3	3.64	-4.7	0.273	0.920	12.2	70.4	32
294.09	57.75	3.72	0.041	0.288	0.301	-4.2	3.91	-4.9	0.327	0.813	15.5	60.3	33

Note:

<sup>1</sup> error on molar fraction is  $100 \left| x_{1,exp} - x_{1,calc} \right| / x_{1,calc}$

<sup>2</sup> error on number of total adsorbed moles is  $100 \left| n_{tot,exp} - n_{tot,calc} \right| / n_{tot,calc}$

<sup>3</sup> average number of iterations in the inner loop

<sup>4</sup> number of iterations in the outer loop



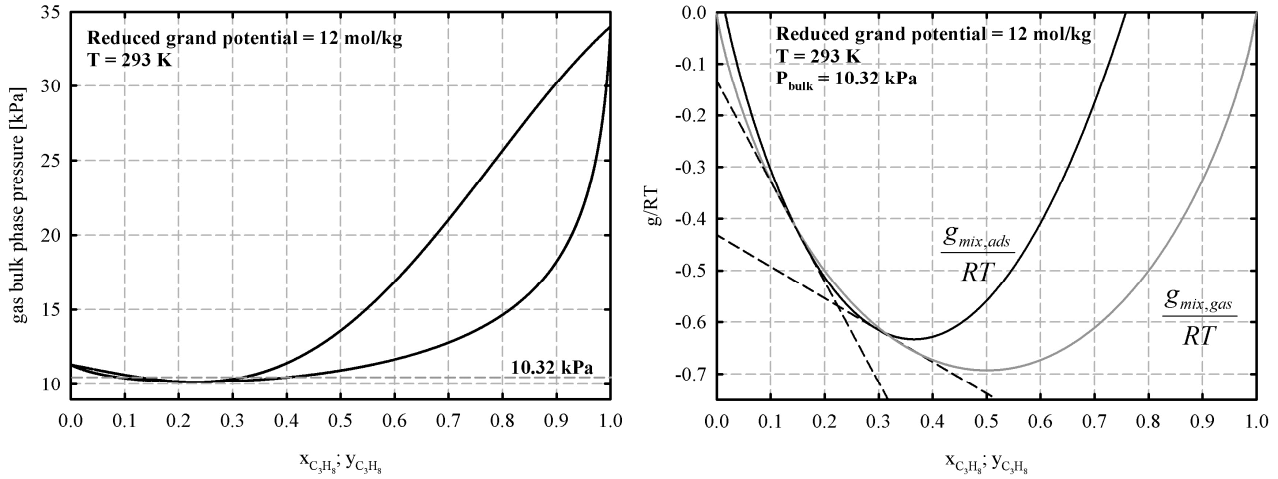


Figure 5. Binary system Carbon Dioxide/Propane on zeolite 13X at 293 K and reduced grand potential  $\psi_{eq}$  of 12.0 mol/kg. P,x,y diagram shows the presence of an azeotropic aggregation state (left) and the concerned  $\Delta g_{mix}$  at 10.32 kPa (right)

### 5. Common tangent approach for non-ideal adsorption at high pressures

In this case adsorption of the Methane(1)/Carbon monoxide(2) binary system on activated carbon Norit R1 has been considered [18]. Table 1 reports the parameters for the Dual-site Langmuir isotherm. These parameters have been obtained regressing the absolute amount adsorbed versus the fugacity. In fact, differently from the other cases, here the effect of the bulk molecular density on the adsorption cannot be neglected. So eq. (15) is no longer formulated using surface pressures but directly on fugacities respectively in the bulk phase ( $f_i$ ) and in the adsorbed phase ( $\phi_i^0 P_i^0 = f_i^0$ ). The Soave-Redlich-Kwong equation of state (SRK) has been used to calculate both the fugacities and the densities, coupling it with the ABC equation. In this case the data considered are at constant temperature and, instead of having three parameters, the model has been regressed on only two parameters, respectively  $A_0 = (A+B/T) = -0.0282$  kJ/mol and  $C = 1.503$  kg/mol. The experimental data considered in this case are up to 10026 kPa. Table 5 summarizes the results showing maximal errors on molar fractions and total adsorbed moles respectively of 3.9% and -4.6% and an average number of iterations of 6063.

Table 5: Comparison between experimental data in [18] and results from common tangent plane approach for Methane(1)/Carbon Monoxide(2) binary system on activated carbon Norit R1 at 298 K. Specific pore volume of the solid is  $3.511 \cdot 10^{-4} \text{ m}^3/\text{kg}$ .

$P_{bulk}$ [kPa]	Z	$n_{tot,exp}$ [mol/kg]	$n_{abs}$ [mol/kg]	$y_{1,exp}$	$x_{1,exp}$	$x_{1,calc}$	$x_{1,error}$	$n_{tot,calc}$ [mol/kg]	$n_{tot,error}$	$\phi_1$	$\phi_2$	$\psi_{eq}$ [mol/kg]	$I_{inner}^3$	$I_{outer}^4$
4039.3	0.991	5.13	5.71	0.137	0.331	0.332	0.5	5.55	-2.8	0.946	0.996	10.6	277.2	28
5067.2	0.990	5.40	6.13	0.136	0.332	0.331	-0.2	6.00	-2.1	0.934	0.995	11.9	454.2	31
5980.7	0.990	5.71	6.56	0.140	0.327	0.338	3.4	6.32	-3.7	0.923	0.995	13.0	319.4	29
1850.0	0.986	4.72	4.98	0.489	0.724	0.750	3.6	4.75	-4.6	0.971	0.999	8.9	141.2	30
2965.0	0.978	5.52	5.95	0.495	0.723	0.751	3.9	5.80	-2.6	0.954	0.999	11.4	120.6	32
4965.0	0.966	6.31	7.03	0.499	0.728	0.755	3.7	6.92	-1.7	0.926	1.000	14.7	117.2	33
7103.0	0.910	7.01	8.11	0.894	0.961	0.964	0.3	8.38	3.3	0.892	1.019	20.1	139.1	33
8066.0	0.901	7.08	8.35	0.895	0.961	0.965	0.3	8.60	3.0	0.880	1.024	21.2	120.0	33
9045.0	0.893	7.10	8.53	0.895	0.957	0.965	0.8	8.79	3.0	0.868	1.029	22.2	118.7	32
10026.0	0.886	7.14	8.74	0.895	0.963	0.965	0.2	8.94	2.3	0.857	1.034	23.1	117.2	34

Note:

<sup>1</sup> error on molar fraction is  $100 |x_{1,exp} - x_{1,calc}| / x_{1,calc}$

<sup>2</sup> error on number of total adsorbed moles is  $100 |n_{tot,exp} - n_{tot,calc}| / n_{tot,calc}$

<sup>3</sup> average number of iterations in the inner loop

<sup>4</sup> number of iterations in the outer loop

In all the cases considered, the isofugacity condition provides solutions identical to those of the CTP approach. This is because, differently to a VLE flash calculation, in an adsorption equilibrium, both  $P_{bulk}$  and the composition of the bulk gas phase ( $y_i$ ) are given. In this case the fugacity coefficients of the bulk gas phase can be directly calculated, resulting in a constant value for the left hand side of eq. (5), instead of a

function of the compositions. This feature reduces the chances of having multiple solutions for the isofugacity condition.

## 6. Example of multiple solutions from isofugacity approach

A final hypothetical binary system is proposed involving two Langmuir isotherms and the ABC equation. It shows how the multiple solutions can be obtained from the isofugacity condition. Fig. 6 illustrates graphically this feature. The two curves are a representation of the two equations solving the isofugacity condition. They intersect in three points, suggesting three possible compositions for adsorbed phase equilibrium. Conversely,  $\Delta g_{\text{mix}}$  and its common tangent plane exhibit only the thermodynamically consistent solution (Fig. 7). In this case, the adoption of the common tangent plane approach is mandatory to obtain the correct solution unless high quality initial guesses are used to solve the isofugacity condition.

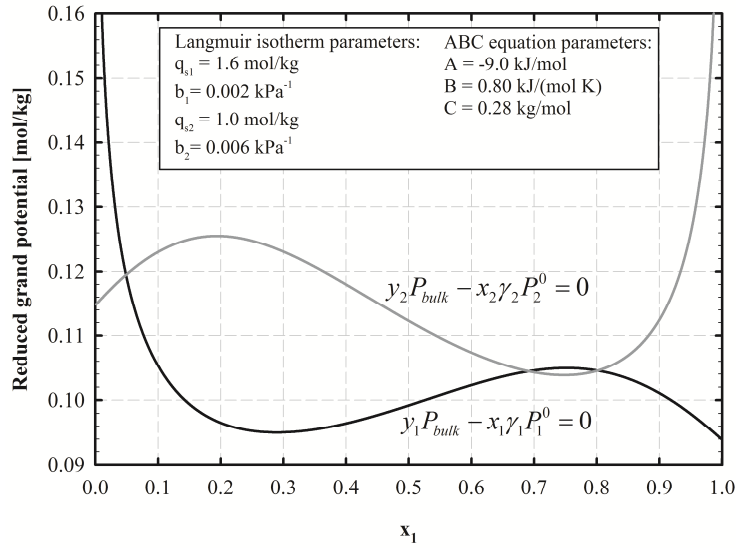


Figure 6: Isofugacity system of equation showing three roots for the equilibrium composition of the adsorbed phase at  $T = 295 \text{ K}$ ;  $P_{\text{bulk}} = 101.325 \text{ kPa}$  and  $y_1 = 0.8$ ;

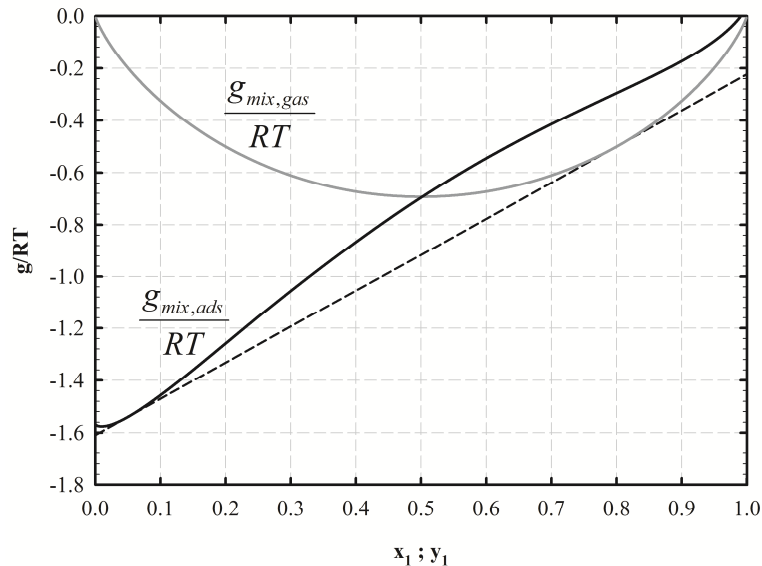


Figure 7: The common tangent plane of  $\Delta g_{\text{mix}}$  locates only one solution for the problem of Fig. 6.

## 7. Conclusions

The common tangent plane approach has been successfully extended to adsorbed solutions. This approach generally applied to VLE calculations cannot be applied in the same way to the adsorbed solutions because of the presence of an additional independent variable, the reduced grand potential. A bilevel algorithm has been adopted to solve this problem and to determine the common tangent plane of the Gibbs energy of

268 mixing. An ideal case, a non-ideal azeotropic system case and a non-ideal high pressure case illustrated the  
 269 application of the common tangent approach to adsorbed solutions. For the ideal case the approach has been  
 270 validated on experimental data and on the direct solution of IAST providing respectively low error and  
 271 identical results. The non-ideal cases have been validated by comparison of the results with experimental  
 272 data and applying respectively the Virial and the Soave-Redlich-Kwong equations of state to take into  
 273 account fluid-fluid interactions in the bulk gas phase. A Gibbs energy excess model (ABC equation) for  
 274 fluid-solid interactions in the adsorbed phase was also considered. The existence of a common tangent plane  
 275 is a necessary and sufficient condition for equilibrium which is valid also in the adsorbed solution theory as  
 276 demonstrated in a conclusive example.

277

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 282 AMPGas.

283

## 284 **Nomenclature**

285	$f_i$	Fugacity of component $i$ [kPa]
286	$f_i^0$	Fugacity of pure component $i$ at the system temperature and pressure [kPa]
287	$g_{ex}$	Excess Gibbs energy [kJ/mol]
288	$g_{mix,ads}$	Branch of the Gibbs energy of mixing function (adsorbed phase) [kJ/mol]
289	$g_{mix,gas}$	Branch of the Gibbs energy of mixing function (bulk gas phase) [kJ/mol]
290	$\Delta g_{mix}$	Molar Gibbs energy of mixing [kJ/mol]
291	NC	Number of components participating in the adsorption
292	$n_i$	Specific absolute amount adsorbed of component $i$ [mol/kg]
293	$n_{tot}$	Specific amount of total adsorbed moles [mol/kg]
294	$P$	Pressure [kPa]
295	$P_{bulk}$	Pressure of the mixture in the bulk gas phase [kPa]
296	$P_i^0$	Surface pressure of the component $i$ [kPa]
297	$R$	Universal gas constant [kJ/(mol K)]
298	$T$	Equilibrium temperature [K]
299	$w_i$	Molar fraction of the component $i$
300	$x_i$	Molar fraction of the component $i$ in the adsorbed mixture
301	$y_i$	Molar fraction of the component $i$ in the bulk gas mixture
302	$Z$	Compressibility factor

303

## 304 **Greek letters**

305	$\gamma_i$	Activity coefficient of component $i$
306	$\phi_i$	Fugacity coefficient of component $i$
307	$\phi_i^0$	Fugacity coefficient of the pure component $i$ in the adsorbed phase at the system temperature
308	and pressure. This is calculated using $P_i^0$	
309	$\psi_{eq}$	Reduced grand potential at equilibrium [mol/kg]
310	$\psi_i$	Reduced grand potential of component $i$ [mol/kg]

311

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